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VI.

ON THE WIDE DIFFUSION OF VANADIUM AND ITS ASSOCIATION WITH PHOSPHORUS IN MANY ROCKS.

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Christian Keferstein, as early as 1834, had boldly stated the proposition that "all crystalline non-stratified rocks, from granite to lava, are products of the transformation of sedimentary strata," and later researches aid in confirming the truthfulness of this view.

Simply considered, all rocks consist of a basis material, generally simple minerals, such as compound silicates, aluminates, or even quartz, in various states of division, united by a compound which acts the part of a cement, which through its composition is more easily acted on by ordinary agents than the particles of the mineral it unites.

This part of every rock engages attention, also, from its acting as a positive compound does in a simple mineral. It is complex in composition, usually it consists of silicates of protoxide bases. At one moment of time it binds the particles with great force; at another, under altered conditions, it relaxes its bonds, itself losing cohesion, crumbling and becoming an earth containing the elements necessary to vegetation, while the bonded materials drop to their condition before union.

Accepting Keferstein's expression in its fullest sense, I have applied the resources of analysis to a large number of rock aggregates, and the results of my experiments have shown the interest and extent of this field of inquiry. To do this, I have departed from the ordinary course of analysis, and applied a principle which, many years since, enabled me accurately to separate alkalies from mineral compounds. This principle is the adaptation of a definite mixture of agents, so that while one part of the mixture is searching for and dissolving the substance to be studied, the other part is holding in a semi-fluid state the larger part of the substance and allowing any reactions or adjustments of composition to take place. The subsequent solution and boiling determines the precipitation of compounds not soluble in the medium. This medium is subsequently decomposed and products divided.

MODE OF ANALYSIS.

The rock perfectly cleansed by washing and brushing, reduced to fine powder, is either dried for its combined water or taken in its natural state. A flux is prepared by melting 202 parts of potassic nitrate with 53 parts of sodic carbonate, both pure. The cooled mass, reduced to powder, absorbs about 0.004 parts when exposed to the air, and must be kept in a closed bottle. This *basis* flux can be adapted to meet all cases of varied composition in minerals. 1 grm. of the rock or mineral is mixed intimately with 1.28 grm. or 2 grms. of this flux in a tall, narrow crucible of platinum, on which no action is exerted. The crucible, covered, is heated over an ordinary Bunsen table lamp, gently while intumescence continues: the heat increased, hissing ceases, a slow sintering follows, and in 12 to 20 minutes the action is over, about one-half the whole power of the lamp being used.

The fused mass, mostly removed from the crucible by a looped platinum wire, with the crucible and cover are boiled in water. The basic silicates, more or less altered, remain; the soluble compounds dissolve, and the filtered solutions and washings, making 40 to 50 CC., are evaporated in a platinum basin to about 6 CC. To the hot solution, ammonic chloride, a little in excess of the equivalent of sodic carbonate used, is added, from a titrated pure solution, the basin put on a water-bath, the contents evaporated, and carefully dried at temperature not exceeding 100° C. After the addition of the ammonic chloride, the silicic acid gelatinizes, and, in drying, passes out of combination with the alkalies. By subsequent boiling in water and filtration, the precipitated silicic compounds are obtained.

The filtrate and washings contain other combinations, which can be treated either in the normal state of acid ammonic salts, or after the addition of a drop of ammonic hydrate renders the solution neutral to test-paper. Numerous cases occur, rendering modifications necessary. Chlorine, bromine, iodine, sulphur, compel a choice of ammonic salts. Many of the acid-forming metals are separated by their characteristic reactions, from the residue of fusion. In general, if the solution of the result of fusion does not deposit silicic acid on the addition of an ammonic salt, 0.25 grm. of silicic acid, with or without its equivalent of sodic carbonate, is added; because the displacement of other acids depends on the presence of an excess of silicic acid. The solution containing nitrites is delicately balanced, but it is always adapted to the statical determination of phosphoric acid by the magnesia mixture, or its estimation volumetrically, in using uranic nitrate. The quantity of phosphoric acid present in mineral or artificial forms of compounds can thus be accurately obtained, and the most compact aggregates do not resist solution.

WIDE DISTRIBUTION OF PHOSPHORUS.

In applying this mode of analysis to a great variety of rocks, it soon became evident that phosphoric acid is widely distributed. In some cases, the basis, as well as the cementing part, of a rock contained it, so that adherence to the plan of seeking it in classified rocks was not possible. Associated with silicates of the more basic earths and the protoxides of metals, it is found in all the clays, the new and old lavas, trachytes, slates, — from the most fissile to the most compact, — shales, ashes of coals; in the rocks formed of quartz, feldspar, and mica; in aggregates where feldspar is replaced by quartzite, and in those containing chlorite. The well-known conglomerates of Roxbury, and a silicious slate reposing near it, contain phosphates.

In the opaque feldspars, the ancient porphyries of Rome and Carthage, phosphates occur; but the glassy and rose-colored varieties have not afforded it. The lepidolite of Paris, Me., contains it; furnace products, slags from copper and zinc, afford it. This list might be extended, without indicating any law relating to the affinities, which may perhaps be discovered as the observations are multiplied. We have in phosphatic salts in rocks another consolidating material, and an element of change.

VANADIUM ASSOCIATED WITH PHOSPHORUS.

In many of the analyses made after the method described, another acid was found associated with phosphoric acid, and this was easily proved to be a compound of *vanadium*. The frequency of its occurrence as acid or oxide, its well-marked characters as a changeful body, the colors of its compounds and mixtures, give great interest to this discovery. Owing to its association with proto salts of manganese and iron in rocks, it proves to be active, first as a binding, and secondly as a disintegrating, agent. It is a matter of surprise that the dissemination of vanadium has not before been noted, especially since its later classification with phosphorus leads to such a conclusion.

When the rocks treated by the above method for phosphoric acid contain manganic compounds, if the second filtrate, balanced by ammonic salts, has any yellow tint, vanadic acid salts are almost surely present. It occurs with phosphoric acid in most of the mineral bodies named above. The physical character of color of the rock is the only indication I now know. The green and plum colors of slates and porphyries; the greenish epidote color of many aggregates; the changed colors, seen in sandstones, and especially in roofing slates, from world-wide localities, are guiding marks merely. My observations have been quite numerous, and as yet no proper *ore* of vanadium has been found, but sources of economical separation have been suggested.

As vanadium occurs in many well-trodden paths, I deemed it important to devise a direct way of obtaining it, in which no metal and the fewest reagents are employed.

PROCESS.

Crush in the diamond mortar 1 to 1½ grms. of greenish slate to a fine and coarse powder; place in a watch crystal, and wet thoroughly with a solution of one-fourth sulphuric hydrate, leaving a little excess. Expose freely to dry, warm air, — sunshine, if possible; and, if the slate is acted on, after 2 to 4 days, when the mass is nearly dry, the salts formed crystallize. Under a lens, a number of green or bluish-black spherical crystalline aggregates, unlike any other matter present, will be seen. These are a double salt, in which blue oxide of vanadium exists; and from such a small weight, often, enough crystals can be picked out for showing the characters of vanadium compounds. It is best to use several differing specimens, which by their colors indicate proto-silicates, and to be sure that they have been carefully washed, as granites are often invested with a lichen of a hemispherical form. One is often surprised to see the number of these crystals extruded from the mass of salt, and formed under constraint. The oxidized rocks do not afford these crystals, but we see bands of yellow vanadium compounds, denoting the condition of the substance.

The ordinary tests of vanadium are best applied to the vanadates, and among them the gall test is delicate and discriminating. If the greenish-black precipitate it forms in acid solutions be burned, the insoluble oxide obtained (when the precipitate is entirely free from any chloride) has characteristic reactions with acids, and in the blowpipe flame with fluxes. The salts of vanadium in mixture with manganous salts, precipitated by excess of ammonic hydrate, afford a blue solution above the oxides, rivalling that of cupric oxide.

By oxidizing the blackish-blue salt obtained by sulphuric hydrate, the yellow compounds form, and may be tested under both modifications.

The vanadate of ammonia present in the balanced solution from the silicates, by the mode of analysis described above, may be separated by over-saturating the solution with ammonic chloride, when ammonic vanadate separates; although phosphoric acid is present. From the vanadate other combinations of vanadium may be formed. The solution does not then respond to the gall test; and the ammonic vanadate separated, when heated, leaves vanadic acid. The deposit caused by tinct. galls may be calcined for VO^2. In testing for phosphoric acid, in this mixed solution, the magnesia mixture does not respond at once, unless the device of Wollaston be used; and, in strong solutions, plumose vanadates form. If heat is applied to the salts in mixture with chlorides, much of the vanadium will be lost. In most of the rocks containing phosphorus, vanadium has been found associated. Manganese is also a congener; and, without repeating here the list of rocks, I can promise in a future paper to give a tabulated series.

In Utah, in the Tintic District, there is a chalcedonic rock, with brown ferric and cupric ore. In the brown part of this ore both phosphorus and vanadium are abundant. The presence of vanadium, in crusts on copper rock of Lake Superior, announced some years since, by my late friend, J. E. Teschemacher, has been lately confirmed. It is present in light grayish earth-like substance of the datholite beds in the Calumet and Hecla mines. At present it appears that vanadium is as common a constituent of rocks as manganese.

VANADIC COMPOUNDS IN WATER.

The beautiful suburb of Boston, Brookline, owes its varied surface and scenic effect largely to *water action* in forming the gravel drift into elevations and depressions, having curved and graceful lines. This drift presents us with a magazine of rock aggregates, which not only supply the laboratory, but, in various cuttings, allow us to watch the influence of air, frost, and water on the rocks; which, stable in their beds, become changed, even rapidly, on exposure to these agencies. This gravel, permeated by air, changing under every variation of pressure, is powerfully oxidizing; and the rain water, even if colored on entering it, becomes colorless and sparkling at eight yards below the surface. The gravel contains strata and inclined dykes of extremely finely divided micaceous earth, or "quicksand," in which the water circulates and passes to the ocean at different levels. An *average* result of partial analyses is: 1 litre affords by evaporation and drying at 100° 0.350 grm., of this amount 0.182 grm. is nearly insoluble matter; 0.168 grm. again dissolves in water, and contains, besides the ordinary salts, soluble silicates, not altered by boiling, drying, or heat of 100° C. These waters attack crystal glass, leaving an incrustation, which resists weak acids; and they seem to be free to act in re-consolidating strata. Indeed, in the deep parts of the gravel deposits, we meet with masses of rock in which solution of the silicates in water is hourly going on; and we may follow these solutions to the wells, and observe that sometimes depositions are formed on the surfaces of the rocks, over which they pass.

Vanadium exists in the water, which supplies the wells of the district of the drift, as a transparent, colorless solution of magnesian calcic, manganous, and ferrous silioates, phosphates, carbonates, and vanadates.

The deposit which forms in the boiling water resembles in composition the matter as taken from rocks by weak solvents, although some of these compounds remain dissolved in the water after it has been boiled.

Detection of vanadium as oxide is easily and at once effected, by dissolving the deposit formed from boiling water, by means of diluted nitric or sulphuric hydrate. In this solution, the addition of a slight excess of ammonic hydrate, and a moment after a considerable excess of ammonic carbonate, insures the reduction of any vanadic compound, by the manganous and ferrous oxides, and separation of other compounds than magnesic oxide and the blue vanadous oxide, which appears in solution of a rich blue color. In a nearly closed vessel, a bright strip of zinc will withdraw vanadous oxide from the blue solution, at first as a thin bronze coating, then after a black crust.

I believe this is the first discovery of vanadic compounds in water. Before announcing it, every source of error has been scanned; and the labor of connecting the compounds with the rocks where they originate has been performed, as necessary to completeness, in the evidence.

Manganous salts have been observed in waters where humic acid has acted on rocks containing manganous carbonate, and the existence of a water of this kind is known to me; but it must be considered quite apart in composition from a water in which soluble silicates include manganous silicate as part of a compound possessing novel characters.

In concluding this brief account of results proving the existence of phosphates and vanadic compounds in the cementing material of the most common rocks, I wish it to be considered as only introductory to a wide field of interesting research.